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Optical and Photonic Applications of Electroactive and Conducting Polymers

by

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Five-layered symmetrically configured AC light-emitting (SCALE) devices and their three-layered variations: use of gold as an electron and hole injection electrode

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ABSTRACT

Symmetrically configured AC light-emitting (SCALE) devices based on conjugated polymers utilizing indium-tin oxide (ITO) and aluminum as electrodes have been demonstrated recently. Here we report the fabrication of SCALE devices using a more stable high workfunction metal, such as gold, as a charge (both electron and hole) injection electrode. Also, a variation of such devices in which the electroluminescent polymer, instead of being separated from the insulating polymer, is dispersed in the insulating polymer to form a unified emitter-insulator, is reported. These devices emit light in both forward and reverse DC bias with symmetric current-voltage characteristics. Under low frequency AC (sinusoidal) driving voltage, light pulses with double the driving frequency are observed. A model is proposed to account for the device operation.

Keywords: conjugated polymers, light-emitting devices, gold electrode, AC operation

1. INTRODUCTION

Since the first report of electroluminescence in poly(*p*-phenylene vinylene) (PPV),¹ a variety of PPV derivatives and other conjugated polymers and/or copolymers have been found to exhibit electroluminescent properties.²⁻⁴ Lighting-emitting diodes (LEDs) incorporating these materials have demonstrated all the necessary colors (red, green, blue) needed for display. The simplest structure of a polymer LED consists of an emissive layer sandwiched between two electrodes, one of which (usually hole injecting indium-tin oxide, or ITO) is transparent. Such devices typically operate under dc driving fields and the charge injection mechanism has been proposed to be due to Fowler-Nordheim tunneling through barriers set by the difference between the band edges of the polymer and the electrode workfunctions.⁵ In some systems, for example C₆₀,⁶ poly(phenylene acetylene),⁷ and a special PPV derivative,⁸ it was found that the devices actually emit light under reverse dc bias with similar turn on voltages, although some of the devices show unstable electroluminescence (EL) under reverse bias. Also some multiple bilayer structures prepared by dip coating technique show EL under reverse bias.⁹ Recently we have reported the fabrication of symmetrically configured AC light-emitting (SCALE) devices based on poly(*p*-pyridine) (PPy) and poly(*p*-pyridyl vinylene) (PPyV) by introducing two "insulating" layers sandwiching the emitting layer.¹⁰ The SCALE devices emit light under both forward and reverse dc bias as well as AC driving voltage. Under AC (sinusoidal) driving, light pulses with double the driving frequency are generated. This

unusual behavior has been attributed to the effects of the interface states created by the introduction of the insulating polymer. In the initially reported SCALE devices, emeraldine base (EB) form of polyaniline and poly(methylmethacrylate) (PMMA) were used as the insulating materials, ITO aluminum (Al), and even gold (Au) were utilized for electrodes, and the insulating layers were separated from the electroluminescent layer. Also SCALE devices using a copolymer of PPV and PPyV, poly(2,5-dihexdecanoxy phenylene vinylene pyridyl vinylene) (PPV.PPyV) have been reported.^{11,12} Variation of the SCALE device also has been reported using poly(3-hexyl thiophene) (P3HT) as the insulating material and, for some devices, high workfunction metal copper (Cu) instead of Al for one of the contacts.^{11,12} Here we present details of the fabrication of SCALE devices using ITO and gold (Au) as electrodes, and also a new type of AC light-emitting devices in which the EL polymer is dispersed in an insulating polymer to form a unified emitter-insulator. In both cases, the devices can be operated in both forward and reverse bias as well as in AC mode.

2. EXPERIMENTAL

The syntheses of PPy¹³ and EB¹⁴ have been reported previously. For the 5-layered SCALE device ITO/EB/PPy/EB/Au, EB and PPy films were spin-cast from solutions in N-methylpyrrolidinone (NMP) and in formic acid, respectively, at ~2000 rpm. For the 3-layered AC device ITO/emitter-insulator blend/Al, the emitter-insulator blend was prepared by mixing a solution of PPy in formic acid and a solution of Nylon 6,6 in formic acid. The weight ratio of PPy to Nylon 6,6 is approximately 1:10. The final solution concentration is ~ 1%. The emitter-insulator layer is similarly spin-cast. Before spin-coating, the ITO substrates with sheet resistance of ~20 Ω/\square were ultrasonically pre-cleaned in isopropyl alcohol, blown dry with nitrogen gas and irradiated in a UV-ozone chamber for approximately 10 minutes. The resulting polymer film thicknesses are approximately 1000 Å each as measured by a Dektak surface profilometer. The Au or Al electrodes were deposited by vacuum evaporation at a pressure of ~ 10^{-6} torr. To prevent damage to the polymer films, the substrates were mounted on a cold water cooled surface during evaporation. Absorption spectra were measured on spin-cast films using a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrometer. Photoluminescence and electroluminescence were measured using a SPEX Fluorolog Fluorometer. The I-V characteristics were measured using two Keithley 195A multimeters while dc voltage was applied by a HP 6218A dc power supply. Under AC driving the sinusoidal voltage was supplied by a HP 3311A function generator. The EL intensity was measured and recorded using a photomultiplier (PMT) (Hamamatsu Photonics, type R928) and a Tektronics 2430A oscilloscope.

3. EXPERIMENTAL RESULTS

Figure 1 shows the absorption spectra of a PPy film spin-cast from solution in formic acid and a EB film spin-cast from solution in NMP, as compared to the photoluminescence (PL) spectrum of a PPy film. To simulate the device fabrication process, the EB film was spun from NMP solution and then "spin-coated" with formic acid. The PL of PPy peak at ~2.35 eV, in the transmission window between the two strong absorption bands of EB, is apparently shifted with respect to the PPy absorption peak (~3.35 eV).

Figure 2 compares the I-V characteristics for EB/PPy/EB SCALE devices utilizing ITO/Al and ITO/Au as electrode pairs. The two devices emit light under both forward and reverse bias, and show similar I-V characteristics with similar turn on voltages despite the fact that Al and Au have much different workfunctions (4.2 eV vs 5.3 eV). Note that the thickness of the EB layer in the Au device is thicker than that in the Al device, which may account for the slightly higher turn on voltage in the Au device. (The motivation for thicker EB in the

Au device is reduction of diffusion of Au into the emitter layer). Under low frequency AC (sinusoidal) driving voltage, light pulses with twice the driving frequency were observed. Fig. 3 shows the variation of the EL intensity of a ITO/EB/PPy/EB/Al device driven by a 60 Hz sinusoidal voltage. A similar result was observed for the ITO/EB/PPy/EB/Au device. The I-V characteristics for the 3-layered ITO/PPy-Nylon 6,6/Al device are shown in Fig. 4. This device works well under both forward and reverse bias.

4. DISCUSSION

The charge injection mechanism for polymer LEDs is usually represented by a very simplified model, within which the polymer/electrode interface is assumed to be an abrupt separation between two media with no localized electronic states (interface states). As a consequence, the I-V characteristics for most polymer LEDs have been proposed to be controlled only by a workfunction related mechanism.⁵ However, a vast amount of work on semiconductors has shown that this often is not true.^{15,16} The symmetric I-V curves, which are not sensitive to the electrode workfunction, for the SCALE devices reported here suggest that the interfaces play an important role in the device operation, particularly the polymer/polymer interfaces. The workfunction of Au is ~ 5.3 eV, much higher than that of Al (~ 4.2 eV).² If I-V characteristics for the SCALE devices were controlled by a workfunction related mechanism as in conventional polymer LEDs, dramatically different I-V characteristics are expected when Al is replaced with Au. The similar I-V characteristics for both ITO/EB/PPy/EB/Al and ITO/EB/PPy/EB/Au devices implies that the EB/PPy interfaces are the controlling step of charge injection since the two EB/PPy interfaces are the only unchanged pair of interfaces upon going from the Al device to Au device.

One important aspect of the SCALE devices is that the turn on voltage for the 5-layered ITO/EB/PPy/EB/Al is lower than the corresponding 3-layered devices ITO/PPy/Al with the same thickness of the PPy layer, despite the extra thickness of EB layers. Fig. 5 compares the turn on voltages of four devices with different structures: ITO/PPy/Al; ITO/EB/PPy/Al; ITO/PPy/EB/Al; ITO/EB/PPy/EB/Al. The unusual trend suggests that charge injection from either metal electrode through EB to PPy is easier than to PPy directly. Note that similar behavior has been observed for the SCALE devices based on other polymer systems when EB is used as the insulating polymer.^{11,12} This is not surprising since EB as a redox polymer, can accept electrons (or holes) easily to vary its oxidation states reversibly. Specifically, the available negative and positive polaron levels within the π - π^* band gap may play an important role in charge injection and transport. We note that while ITO/EB/PPy/EB/Al and ITO/EB/PPy/Al devices emit light in both forward and reverse bias, no light (or very weak light) was observed for ITO/PPy/Al and ITO/PPy/EB/Al devices under reverse bias, indicating that electron injection from ITO to PPy is the main efficiency limiting step in the device operation under reverse bias.

We propose the following mechanism for the SCALE device operation.¹⁰ Under low bias voltage, electrons and holes are injected from the electrodes to the quinoid and benzenoid levels of EB and form negative and positive polarons, respectively. These polarons transport to the EB/PPy interfaces via a hopping mechanism and populate the EB/PPy interfaces. When the applied electric field is high enough, the stored charges begin to tunnel into the conduction and valence bands of PPy. The injected charges may form intrachain exciton and decay radiatively to emit photons or follow other nonradiative decay paths. Because the polarons levels are within the π - π^* band gap of EB, and are also likely within the band gap of PPy, the barriers for charge injection from electrodes to polaron levels of EB are significantly reduced as compared to injection directly to conduction and valence bands of PPy. The limiting barriers for charge injection are no longer the electrode/polymer contacts as proposed⁵ for conventional polymer LEDs but now the polymer/polymer (EB/PPy) interfaces of the SCALE

devices. Due to the inter-penetrating network structure of the polymer/polymer interfaces, non-uniform electric fields are created making charge injection easier, hence reducing the overall barrier height. This argument is supported by the lower turn on voltages of the SCALE devices as compared to the corresponding conventional devices. The non-uniform electric field effect is clearly demonstrated in PPV devices using high-surface area network conducting polyaniline as hole injection electrode.¹⁷ If the charge injection is not balanced, as is the case for most polymer LEDs, the excess charge carriers may migrate through the PPy layer without decaying. Most of these charges will be trapped in the opposite PPy/EB interface. It is suggested that these trapped charges enhance the electric field of the nearby EB layer, and thus enhance the minority charge injection from the electrode, improving the device efficiency. When the bias voltage is reversed, the shallow trapped charges will be released from the interfaces and contribute to the recombination current. The deep trapped charges which act as quenchers or injection limiters in DC devices will be neutralized. We point out that the use of stable high workfunction metals, such as Au, as electrodes to inject both electrons and holes for the SCALE devices may reduce the problems of aging of contacts of polymer light-emitting devices.

The 3-layered ITO/PPy-Nylon/Al device can be understood as a variation of the SCALE device. In this case, the emitter/insulator interfaces, instead of being sharply defined, are spread throughout the polymer layer. For devices that have a small fraction of emitter polymer, e.g. 1:10 ratio of PPy to Nylon for the device of Fig. 4, the limiting step for charge injection is likely tunneling from the electrodes through insulating polymer (Nylon) (instead of hopping as for EB), since in this case the insulating polymers have very large band gaps (~ 6 eV). It is speculated that at these low loadings, the emitter polymer network may be excluded from the host insulator (Nylon) polymer at the polymer/electrode interfaces, causing the above mentioned charge injection to be the limiting step.

5. CONCLUSION

It is concluded that interfaces play an important role in the SCALE device operation, particularly the emitter/insulator interfaces. When EB is used as the insulating polymer, the reduction of the charge injection barriers at the EB/electrode interfaces allows the use of stable high workfunction metals, e.g. Au, as charge injection electrodes, which may reduce the problems of aging of contacts of polymer light-emitting devices.

5. ACKNOWLEDGMENT

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6. REFERENCES

1. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, "Light-emitting diodes based on conjugated polymers," *Nature*, Vol. 347, pp. 539-541, 1990.
2. D. D. C. Bradley, "Conjugated polymer electroluminescence," *Synth. Met.*, Vol 54, pp. 401-415, 1993.
3. J. Kido, "Organic electroluminescent devices based on polymeric materials," *Trends in Polymer Science*, Vol 2, pp. 350-355, 1994.

4. D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, L. B. Lin, T. L. Gustafson, H. L. Wang, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, "Blue electroluminescent devices based on soluble poly(*p*-pyridine)," *J. Appl. Phys.*, 1995, in press; H. L. Wang, M. J. Marsella, D. K. Fu, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, "Electro- and Photo- luminescent properties of Nitrogen Analogs of PPV: Poly(pyridyl vinylene)," *Polymeric Materials Science and Engineering*, 1995, to be published.
5. I. D. Parker, "Carrier tunneling and device characteristics in polymer light-emitting diodes," *J. Appl. Phys.*, Vol. 75, pp. 1656-1666, 1994.
6. H. J. Byrne, A. T. Werner, W. K. Master, M. Kaser, L. Akselrod, W. W. Ruhle, and S. Roth, "Nonlinear optical and transport properties in fullerene crystals and their relationship to crystal structure," *Proc. Electrochem. Soc.*, San Francisco, USA, 1994, in press.
7. S. A. Jeglinski, M. E. Hollier, J. Gold, Z. V. Vardeny, Y. Ding and T. Barton, "Electrically symmetric poly(phenylene acetylene) diodes," *Mol. Cryst. Liq. Cryst.*, Vol. 256, pp. 555-561, 1994.
8. Z. Yang, B. Hu, and F. E. Karasz, "Polymer electroluminescence using AC or reverse DC bias," *Macromolecules*, 1995, in press.
9. A. C. Fou, O. Onitsuka, M. Ferreira, D. Howie, and M. F. Rubner, "Self-assembled multilayers of electroactive polymers: from highly conducting transparent thin films to light emitting devices," *Polymeric Materials Science and Engineering*, Vol. 72, pp. 160-161, 1995.
10. Y. Z. Wang, D. D. Gebler, L. B. Lin, J. W. Blatchford, S. W. Jessen, H. L. Wang, and A. J. Epstein, "AC driven light-emitting devices based on conjugated polymers," submitted for publication.
11. A. G. MacDiarmid, H. L. Wang, J. W. Park, D. K. Fu, M. J. Marsella, T. M. Swager, Y. Z. Wang, D. D. Gebler, and A. J. Epstein, "Novel light emitting diodes involving heterocyclic aromatic polymers," this proceedings.
12. H. L. Wang, J. W. Park, D. K. Fu, M. J. Marsella, T. M. Swager, A. G. MacDiarmid, Y. Z. Wang, D. D. Gebler, and A. J. Epstein, "Symmetrically configured alternating current light emitting (SCALE) devices: use of copper as an electron- and as a hole- injection electrode," *Polymer Preprints*, 1995, to be published.
13. T. Tamamoto, T. ITO, and K. Kubota, "A soluble poly(arylene) with large degree of depolarization. Poly(2,5-pyridinediyl) prepared by dehalogenation polycondensation of 2,5-dibromopyridine with Ni(0)-complexes," *Chem. Lett.*, pp.153-154, 1988.
14. A. G. MacDiarmid and A. J. Epstein, "Polyanilines: a novel class of conjugated polymers," *Faraday Discuss. Chem. Soc.*, Vol. 88, pp. 317-332, 1989.
15. H. K. Henisch, *Semiconductor Contacts, An approach to ideas and models*, Oxford University Press, Oxford, 1984.
16. E. H. Rhoderick and R. H. Williams, *Metal-Semiconductor Contacts*, Oxford University Press, Oxford, 1988.
17. Y. Yang, E. Westerweele, C. Zhang, P. Smith, and A. J. Heeger, "Enhanced performance of polymer light-emitting diodes using high surface area polyaniline network electrodes," *J. Appl. Phys.*, Vol. 77, pp. 694-698, 1995.

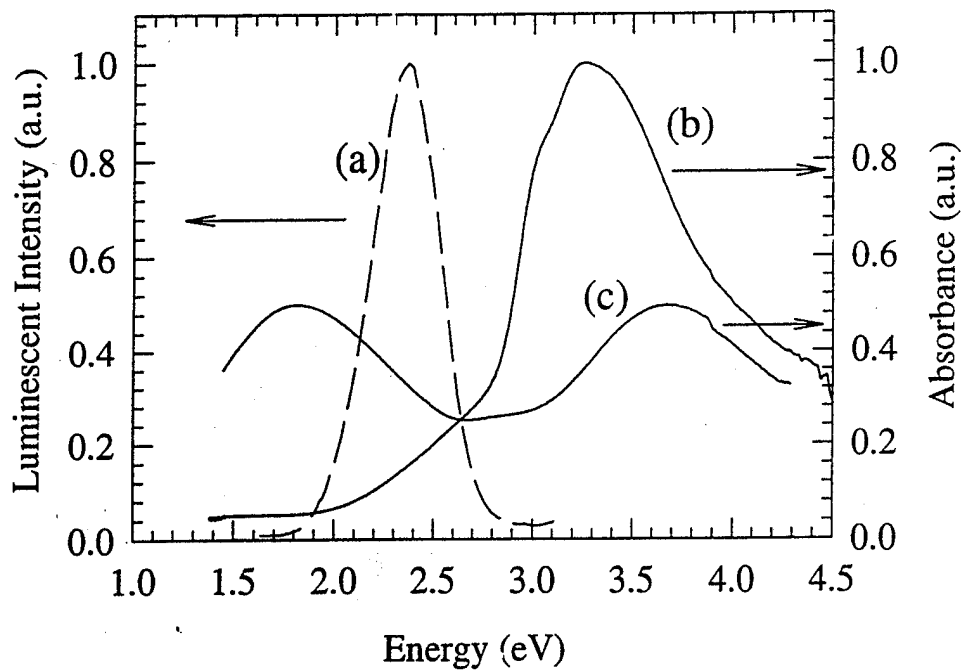


Fig.1. Photoluminescence spectrum (a) and absorbance (b) of a PPy film spun from a formic acid solution and absorbance (c) of an emeraldine base (EB) film spun from NMP and "coated" with formic acid.

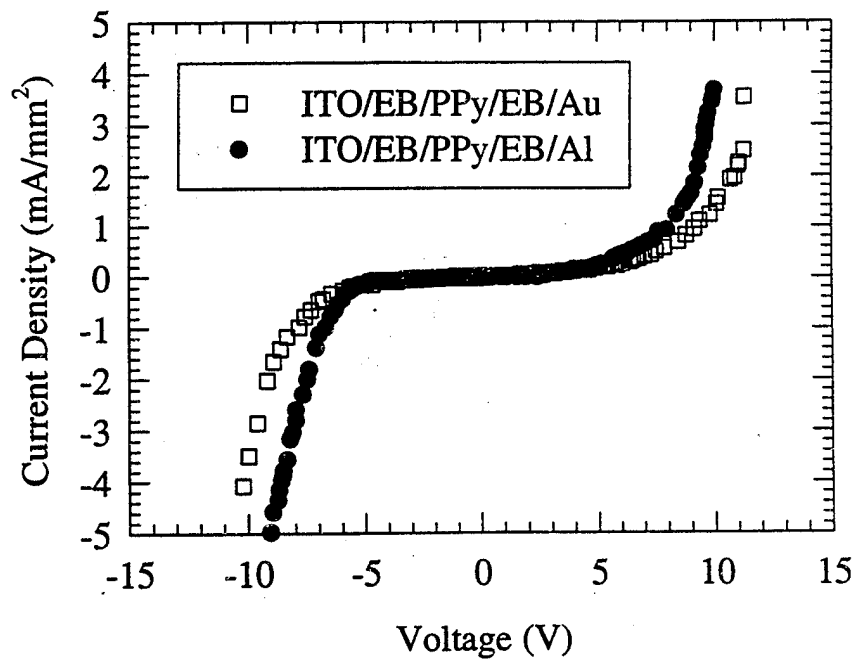


Fig. 2. I-V characteristics of SCALE devices utilizing two different pairs of electrodes ITO/Au and ITO/Al.

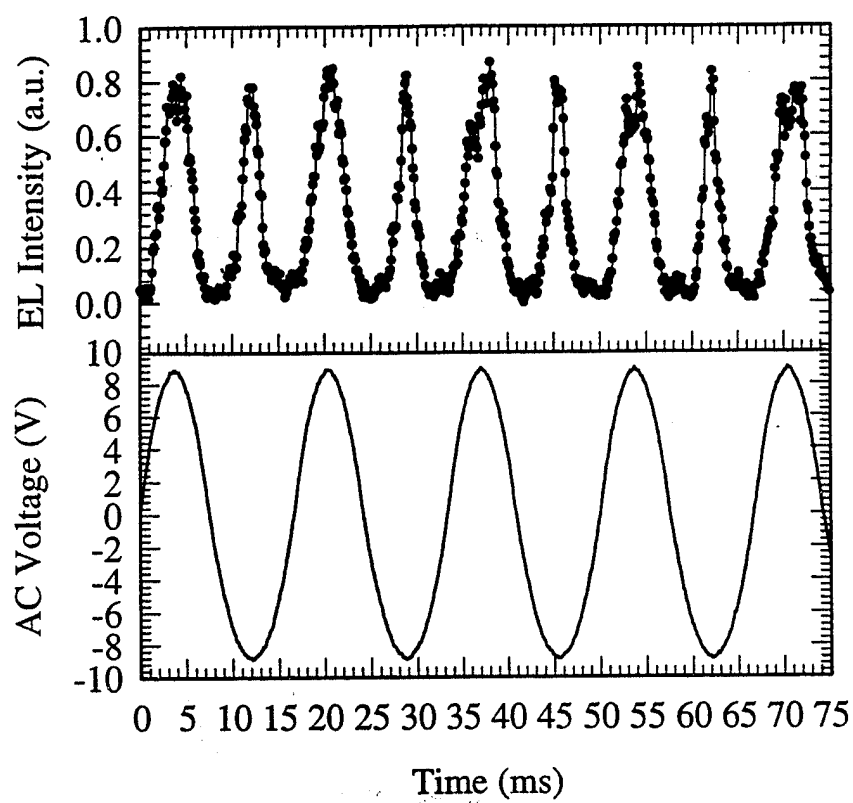


Fig. 3 AC response of a SCALE device ITO/EB/PPy/EB/Al driven by a 60 Hz sinusoidal voltage.

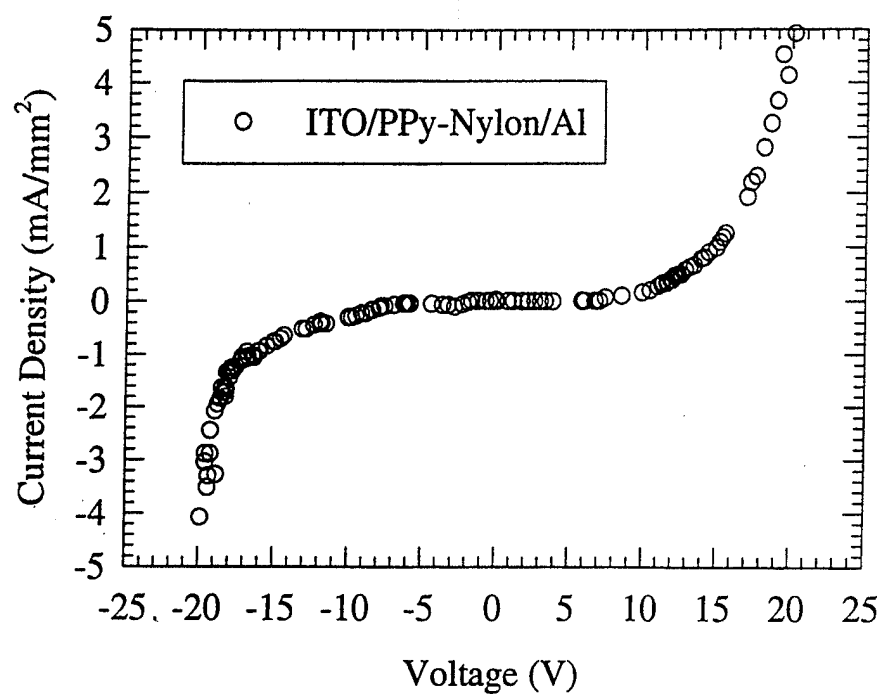


Fig. 4. I-V characteristics of a device where the emitting layer is a blend of PPy and Nylon with a wt:wt ratio of 1:10.

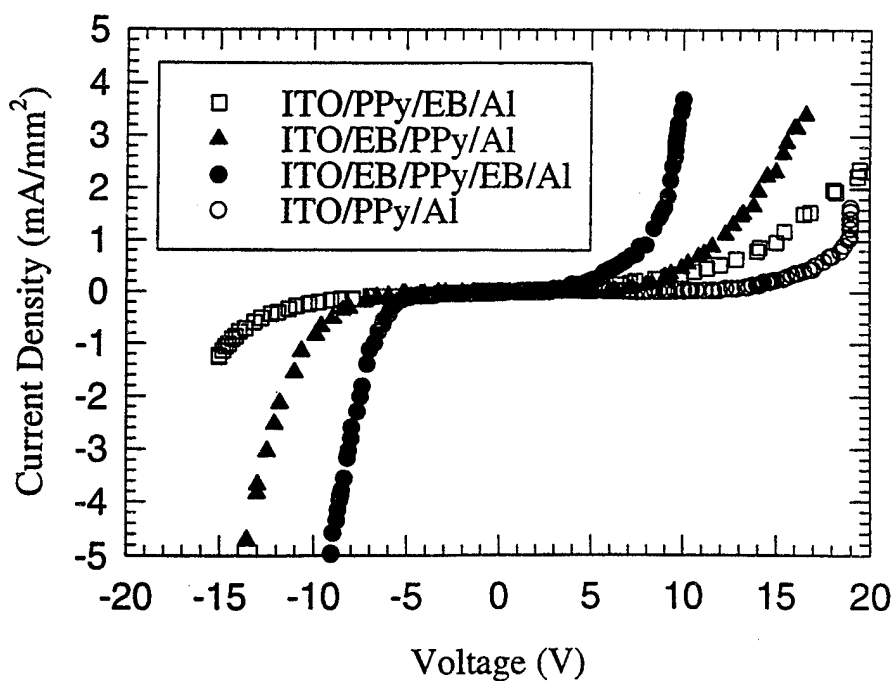


Fig. 5. I-V characteristics of four devices with different structures. Note that the turn on voltage *decreases* as the total number of layers *increases*.